Infrared and Raman Spectra of Single Crystals of Magnus' Green Salt, Tetra-ammineplatinum(II) Tetrachloroplatinate(II)

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The symmetry species of almost all the i.r. and Raman-active vibrations of Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, have been determined from experiments with oriented single crystals. An assignment is proposed, the most important feature being that the A_{2u} lattice mode of the cation–anion chain is placed at 81 and not at 201 cm^{-1} as was previously suggested. The latter band is attributed to NH_3 torsional motion.

MAGNUS' GREEN SALT, $[Pt(NH_3)_4][PtCl_4]$, consists of columnar stacks in which anions and cations alternate.[1] The unusual colour (for Pt^{II}) raises intriguing questions concerning the nature of the interaction between adjacent cations and anions in each chain, and the extent to which it is responsible for the distinctive spectral properties [2] and anisotropic electrical conductivity.[3] The bulk of physical evidence currently favours weak metal–metal interaction, with the exception of one far-i.r. report.[4] Of the various studies of the complex i.r. spectrum of Magnus' green salt,[4-7] the most complete is undoubtedly that of Hiraishi and his co-workers who found *inter alia* that a band at *ca.* 200 cm^{-1} increased substantially in intensity upon cooling with liquid nitrogen. They assigned it to the A_{2u} (in D_{4h}) translational lattice mode (an antisymmetric vibration with vectors along the columnar axis); this band would normally be expected below 100 cm^{-1}, but it was suggested that metal–metal interaction had raised it to *ca.* 200 cm^{-1}. We wished to settle the truth of this proposal by direct determination of the symmetry species of the band, and to prove other points of assignment. We thus report an i.r. absorption study of single crystals of Magnus' green salt (which was of considerable technical difficulty) and the first account of the Raman spectrum of this complex.

EXPERIMENTAL

Crystals of Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, were grown by slow diffusion of the component ions through silica gel.[3] A solution of HCl (2·6M) was added to aqueous sodium metasilicate (1·3M) until pH *ca.* 1 and the solution allowed to gel in a U tube. Solutions of the complexes K_2PtCl_4 (0·2M) and $Pt(NH_3)_4Cl_2,H_2O$ (0·2M) were then added to opposite limbs of this tube. Crystals began to form at the interface within 1 week and were removed after 3 weeks. Those used for the study were *ca.* 2 × 0·5 × 0·5 mm^3. They showed sharp extinctions under the polarising microscope, and had the *c*-axis parallel to the longer side of the specimen.

I.r. spectra were recorded for polyethylene discs of Magnus' green salt (4%), and for a montage of aligned crystals. These were cemented in Araldite on a Rigidex plate with *c*-axes parallel, giving a plate of area *ca.* 4 × 3 mm^2 which was ground to *ca.* 20 μm thickness. The ground surface was inferior in quality to the natural crystal surfaces, ruling out reflectivity measurements. The region 20—600 cm^{-1} was covered using a Beckman-RIIC FS-720 Fourier spectrometer, with a Perkin-Elmer wire-grid polariser. Raman spectra were recorded for oriented crystals using a maximum of 20 mW (488·0 nm) radiation at the sample, with a Coderg PH1 spectrometer and 4 cm^{-1} spectral slit width. A Cryocirc cryostat was used for low-temperature runs. Thermal measurements were made with a Perkin-Elmer DSC 1 differential-scanning calorimeter (we thank Mr. J. Fawcett for these measurements).

RESULTS

I.r. spectra of Magnus' green salt are shown in the Figure; wavenumbers are given in Table 1. The powder sample results were in good agreement with those of Hiraishi and his co-workers. In particular, we confirm that the intensity of the broad band at *ca.* 200 cm^{-1} is markedly enhanced on cooling the sample with liquid nitrogen. Due to difficulty in grinding samples thin enough for transmission measurements, and in packing the crystals closely in Araldite to present a continuous surface, the signal-to-noise ratios of the ' single-crystal ' spectra were inferior to those of the powder spectra. Since there are $11E_u$ modes (Table 2) as opposed to three of A_{2u} type, the signal-to-noise ratios are predictably superior in the E_u spectra. Further improvement was obtained by computer averaging; Figure (*c*) is the average of nine runs. Despite these difficulties, the quality of the final spectra was good and the orientation behaviour of the samples leaves no doubt about the symmetry species of individual bands.

Good-quality Raman spectra were not readily obtained. Experiments with 180° excitation were much less successful than when 90° geometry was used. Apart from a general sharpening of bands, cooling with liquid nitrogen caused no significant alterations to the spectrum observed at ambient temperature, and certainly nothing as pronounced as the behaviour of the 200 cm^{-1} i.r. band.

DISCUSSION

Magnus' green salt has symmetry $P4/mnc$ (D^6_{4h}) with $z = 2$.[1] There are *two* columns in each unit cell, the repeat unit of each being $[Pt(NH_3)_4][PtCl_4]$. Each ion is on a site of symmetry C_{4h}. Correlation coupling between the two columns or chains is described by the

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[4] J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, 1968, **24***A*, 819.

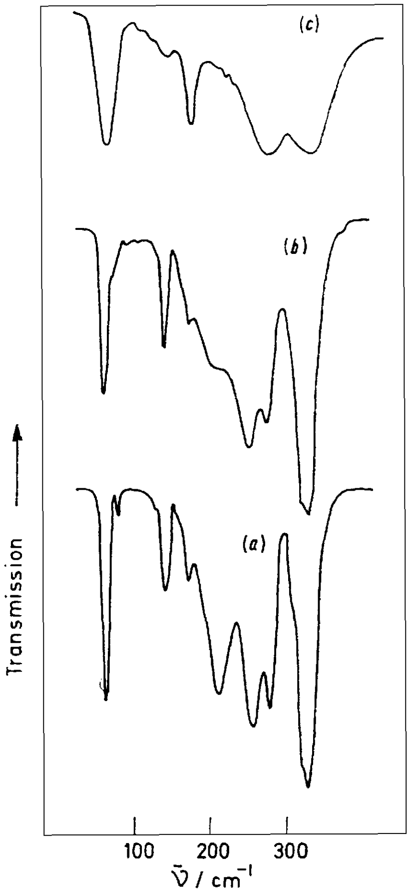
[5] H. Poulet, P. Delorme, and J. P. Mathieu, *Spectrochim. Acta*, 1964, **20**, 1855.

[6] D. M. Adams and D. M. Morris, *Nature*, 1965, **208**, 283.

[7] R. J. H. Clark and C. S. Williams, *J. Chem. Soc. (A)*, 1966, 1425.

scheme in Table 2, which also shows the unit-cell analysis and selection rules.

The A_{2u} *Spectrum.*—The most significant of our results is the observation of *four* bands of A_{2u} symmetry, *viz.* 81, 141, 201, and 241 cm^{-1}; the unit-cell analysis (Table 2) requires only three bands. From the internal-co-ordinate breakdown these are a translatory lattice mode (ν_L) and two complex ion internal modes broadly described as π(Pt–Cl) and π(Pt–N). The 81 cm^{-1} band can only be a lattice mode as neither constituent complex ion has any internal vibrations below 140 cm^{-1} in its salts {*e.g.*, K_2PtCl_4 and $[Pt(NH_3)_4]Cl_2,H_2O$}. In the series of complexes $M_2[PtCl_4]$ the A_{2u} π(Pt–Cl) mode drops from 170 cm^{-1} (M = K) to 146 cm^{-1} (M = Tl),[6,8] typical of the effects noted for complex halide ions upon dilation of the lattice. Consequently, there is little doubt that the band at 141 cm^{-1} is the π(Pt–Cl) mode, lowered in Magnus' green salt by the presence of a large cation. Using similar arguments, the 241 cm^{-1} band is ascribed to the corresponding mode of the tetra-ammine cation, π(Pt–N). Our reasoning therefore leaves the 201 cm^{-1} band to be explained. This is the temperature-sensitive feature which Hiraishi and his co-workers consider to be the A_{2u} translatory mode raised in frequency by Pt–Pt interaction. We have eliminated the possibility that it is associated with a phase change (at least to −100 °C, the limit of the equipment) by showing that there is no specific-heat anomaly. Furthermore, a spectrum run at carbon dioxide–acetone temperature showed the band with intensity roughly midway between those shown at ambient and liquid-nitrogen temperatures.



I.r. spectra of the complex $[Pt(NH_3)_4][PtCl_4]$; (*a*) 4% polyethylene disc at liquid-nitrogen temperature; (*b*) sample (*a*) at ambient temperature; and (*c*) oriented-crystal spectrum (E_u modes)

TABLE 1

Vibrational wavenumbers/cm^{-1} and assignment for the salt $[Pt(NH_3)_4][PtCl_4]$

I.r.[a]		Raman [b]		
Ambient temp.	Liquid-nitrogen temp.	Ambient temp.	Assignment	
		537m	A_{1g}	ν(Pt–N)
		520w	$B_{1g} + B_{2g}$	
502	[c]		E_u	
		315s	A_{1g}	ν(Pt–Cl)
310	310		E_u	
305	306		E_u	
		296w	$B_{1g} + B_{2g}$	
	294		E_u?	δ(Pt–N)
		267w	$B_{1g} + B_{2g}$	
263	266		E_u	
241	245		A_{2u}	π(Pt–N)
201	209		A_{2u}	NH_3 Torsion
		173m	$B_{1g} + B_{2g}$	δ(Pt–Cl)
171	171		E_u	
141	144		A_{2u}	π(Pt–Cl)
81	88		A_{2u}	Lattice modes
71	73		E_u	

[a] For powder samples as polyethylene discs. Single-crystal values are identical with these. [b] From single crystals; relative intensities from powder spectra. [c] Spectrum not run in this region.

TABLE 2

Unit-cell analysis for the salt $[Pt(NH_3)_4][PtCl_4]$ [a]

D_{4h}^6	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u
N_{Total}	4	4	4	4	4	4	4	2	2	12
T_A							1			1
T						2	1			3
R	2	2	0	0	4					
N_i	2	2	4	4	0	2	2	2	2	8
Internal co-ordinates										
ν(Pt–Cl)	1	1	1	1						2
ν(Pt–N)	1	1	1	1						2
δ(Pt–Cl)			1	1						2
δ(Pt–N)			1	1						2
π(Pt–Cl)						1	1	1	1	
π(Pt–N)						1	1	1	1	
Activities	$x^2 + y^2$, z^2		$x^2 - y^2$	xy	(xz,yz)		z			(x,y)

Correlation

Free ion	Site		Crystal
D_{4h}	C_{4h}	$\xrightarrow{\times 2}$	D_{4h}
A_{1g}	A_g		$A_{1g} + A_{2g}$
B_{1g}	B_g		$B_{1g} + B_{2g}$
B_{2g}	B_g		$B_{1g} + B_{2g}$
A_{2u}	A_u		$A_{1u} + A_{2u}$
B_{2u}	B_u		$B_{1u} + B_{2u}$
E_u	$2E_u$		$2E_u$

Modes: T_A, acoustic; T, translatory; R, rotatory; and N_i, internal.

[a] Hydrogen atoms were neglected.

We consider that 201 cm^{-1} is unrealistically high for a

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[8] D. M. Morris, Ph.D. Thesis, University of Leicester, 1967.

translatory lattice mode involving anti-phase motion of cations and anions having masses 263 and 337 respectively. Treating a single chain of Magnus' green salt as a linear diatomic polymer, there is only one non-acoustic translatory longitudinal mode, A_u, in C_{4h}. In the unit cell, two such modes couple in and out of phase giving A_{1u} (inactive) + A_{2u} (i.r.) in D_{4h}^6. The A_u mode has frequency $\nu = (1/2\pi)(2f/\mu)^{\frac{1}{2}}$, where μ is the reduced mass and f the force constant. For the 201 cm^{-1} band, $f = 1{\cdot}76$ dyn cm^{-1}. This may be compared with a force constant of 1·6 dyn cm^{-1} for the complex $[Re_2(CO)_{10}]$,[9] obtained by treating it as a diatomic molecule with masses of $M/2$. In other words, the 201 cm^{-1} mode, if assigned as the A_{2u} lattice mode, implies a Pt–Pt bond strength comparable with that of the metal–metal bond in the complex $[Re_2(CO)_{10}]$. Our assignment of ν_L at 81 cm^{-1} requires $f = 0{\cdot}07$ dyn cm^{-1}, a value comparable with those found by normal-co-ordinate analysis of complex ionic materials.[10] Circumstantial evidence for the marginal nature of the Pt–Pt interaction is provided by the observation that mixing the constituent ions sometimes yields Magnus' green salt and sometimes the pink isomer;[11] the latter is readily converted to Magnus' green salt. We conclude that Hiraishi and his co-workers were misled in their assignment of the 201 cm^{-1} band, even though we have shown its symmetry species to be compatible with their suggestion.

In accounting for the 201 cm^{-1} band of Magnus' green salt, we note that a similar feature is exhibited by the salt $[Pt(NH_3)_4][PtBr_4]$ and is only 11 cm^{-1} lower than that in Magnus' green salt.[4] If a translatory mode were responsible, addition of 178 mass units would be expected to result in far greater depression of its value. These facts are accommodated by the suggestion that the temperature-sensitive band is associated with NH_3 torsional motion. We note that Sheppard and his co-workers[12] estimated the barrier to NH_3 rotation in the solid complex *trans*-$[PdCl_2(NH_3)_2]$ as 225 cm^{-1}. Hiraishi and his co-workers showed that the complex *trans*-$[PtCl_2(NH_3)_2]$ does not exhibit a strongly temperature-sensitive band at *ca.* 200 cm^{-1}.[4] However, it should be noted that both NH_3 torsions in an isolated molecule of the diammine complex are inactive; although they *can* become active in the crystal they can only do so by means of the site symmetry (C_i).[13] We therefore consider the evidence from this spectrum to support our arguments.

The hydrogen atoms in Magnus' green salt can be placed upon more than one set of Wyckoff sites (in the absence of direct determination of their positions). The resulting reduced representation for NH_3 torsions is therefore dependent on which set of sites are chosen. However, in any model *some* of the atoms must be on general sites; the representation then inevitably spans both A_{2u} and E_u species. In practice we observe that the A_{2u} character predominates.

Finally, possible explanations of the 201 cm^{-1} band in terms of combinations should be considered. Overtones cannot be i.r.-active in D_{4h} and the only allowed combinations are between i.r.- and Raman-active modes. The A_{2u} nature of the band can be accommodated only by the products $A_{1g} \times A_{2u}$, $B_{1g} \times B_{2u}$, $B_{2g} \times B_{1u}$, $A_{2g} \times A_{1u}$, and $E_g \times E_u$. The second, third, and fourth possibilities involve combination with one or more inactive modes and seem improbable; using either of the other two involves combination of an internal mode with an unobserved lattice mode of rotatory type. We believe our above interpretation in terms of NH_3 torsions is the more realistic.

The E$_u$ *Spectrum.*—This spectrum is evidently incomplete. The correlation scheme shows that two E_u modes should be found in both ν(Pt–N) and ν(Pt–Cl) regions. Only one ν(Pt–N) band was found, but the ν(Pt–Cl) band had a shoulder at 306 cm^{-1} which could be either the second E_u mode or, more probably, ν(Pt–^{37}Cl). We think it probable that the correlation field is too weak to split the two E_u modes from each other in either case. It remains to account for the four E_u in-plane bending modes. One appears to be at 294 cm^{-1}, *viz.* the weak shoulder on ν(Pt–Cl); we could not determine its symmetry species. Hiraishi and his co-workers[4] report a band at 298 cm^{-1} in $[Pt(NH_3)_4][PtBr_4]$, which supports the above assignment to an E_u δ(Pt–N) mode at 294 cm^{-1}. Two more E_u modes are at 266 and 171 cm^{-1} and are assigned as in Table 1; the fourth is missing. Only one out of the three predicted E_u lattice modes was observed to a lower limit of 20 cm^{-1}.

Raman Spectrum.—The (xz) and yz) spectra were featureless, indicating that (a) the extinctions between these and other orientations are good, and (b) the four E_g rotatory lattice modes are either not higher than 30 cm^{-1} or are vanishingly weak. Similarly, there was no evidence in the (yy) spectrum for the two low-frequency rotatory modes predicted. The two observed A_{1g} bands clearly correspond to ν(Pt–N) (537 cm^{-1}) and ν(Pt–Cl) (315 cm^{-1}). Bands at 520 and 296 cm^{-1}, assigned as in Table 1, are of $B_{1g} + B_{2g}$ symmetry. The two lower bands (173 and 267 cm^{-1}) are two of the four expected in-plane bends with the missing contributions probably coincident with those observed since they can only differ physically by means of the correlation field.

CONCLUSION

The assignment for Magnus' green salt has been considerably strengthened by single-crystal i.r. and Raman measurements. It is now clear that the i.r. evidence can be understood without the need to postulate strong metal–metal interaction. Some ambiguities

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[12] R. C. Leech, D. B. Powell, and N. Sheppard, *Spectrochim. Acta*, 1965, **21**, 559.

[13] G. H. W. Milburn and M. R. Truter, *J. Chem. Soc.* (*A*), 1966, 1609.

remain; in an attempt to resolve them we are currently growing crystals of $[Pt(NH_3)_4][PtBr_4]$ and of one deuteriate.

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